学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Electrocatalytic Nitrate and Nitrous Oxide Reduction Reactions at Trimetallic Interfaces of Pt, Pd and Sn
（白金，パラジウム，スズの三元金属界面における硝酸イオンおよび亜酸化窒素の電極触媒還元反応）

Nitrate anion (NO_3^-) contamination in groundwater, which is mainly caused by agriculture and industrial effluents, has a negative effect on the environment and human health, such as methemoglobinemia (blue baby syndrome) and human cancer. The electrocatalytic NO_3^- removal is the most promising technique, in which NO_3^- can be reduced to harmless dinitrogen (N_2) with many by-products: nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), ammonium ion (NH_4^+), and hydroxylammonium ion (NH_3OH^+). N_2O is a potential by-product, which is accountable for global warming and the depletion of the ozone layer. Therefore, efficient electrocatalysts are needed to develop for both NO_3^- reduction reaction (NO_3RR) and N_2O reduction reaction (N_2ORR). In the previous studies, Sn-modified Pt and Pd electrodes were widely studied for NO_3RR but the same electrode was not studied for the reduction of NO_3^- and its potential by-products: NO_2^-, NO, and N_2O. In a reverse system, only Pt nanoparticle (NP)-modified fluorine-doped tin oxide (FTO) substrate electrodes (Pt/FTO) were studied for NO_3RR, in which the Pt/Sn interface catalyzed the reaction. Therefore, the objective of this thesis is to expand the investigation on (i) the reverse system: (Pt+Pd) mixture NP-modified FTO electrodes and (ii) chemically synthesized Pt–Pd–Sn NP electrodes for the reduction of NO_3^- and its potential by-products: NO_2^-, NO, and N_2O. This thesis includes five chapters. Chapter 1 describes those backgrounds and the objective of this study, and the conclusions were summarized in Chapter 5.

In Chapter 2, the Pt and/or Pd NPs on FTO substrate electrodes: Pt/FTO, Pd/FTO, and Pt/Pd/FTO were prepared by an arc-plasma deposition (APD) method and investigated for the electrocatalytic reduction of NO_3^-, NO_2^-, NO, and N_2O in acidic media by cyclic voltammetry (CV). The trimetallic PtPd/Sn interface of the Pt/Pd/FTO electrode with Pt:Pd = 3:2 atomic ratio showed higher catalytic activity than the bimetallic Pt/Sn or Pd/Sn interface for the NO_3RR and N_2ORR, whereas the PtPd/Sn interface showed no drastic contribution to the electrocatalytic NO_2^- and NO reduction reactions. Because the NO_3^- and N_2O reduction reactions occur in the potential region of H-adsorption on Pt and Pd electrodes, the PtPd/Sn interface could enhance NO_3^- and N_2O adsorption and/or suppress the H-adsorption.

In Chapter 3, Pt–Sn and Pt–Pd–Sn NPs with the optimized Pt:Pd = 3:2 atomic ratio obtained from the APD method were synthesized and investigated for the electrocatalytic N_2ORR in acidic media by CV. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy dispersive spectroscopy (EDS) mapping images confirmed the formation of Pt@Sn and Pt–Pd@Sn core@shell NPs. The trimetallic Pt–Pd–Sn NPs showed higher N_2ORR activity than the bimetallic Pt–Sn NPs. The suppression of H-adsorption was confirmed from the lower Faradaic efficiency of H_2 at the PtPd/Sn interface than that at the Pt/Sn interface at 0.0 V vs. RHE, resulting in the high N_2ORR activity. The PtPd/Sn interface showed turnover frequency (TOF) of 5.29 $\mathrm{mol}_{\mathrm{N}_2}\ \mathrm{mol}_{(\mathrm{Pt+Pd})}^{-1}\ \mathrm{min}^{-1}$ for the N_2ORR to N_2 with about 100% Faradaic efficiency at +0.06 V vs. RHE.

In Chapter 4, Pd nanocubes (NCs) on carbon support were prepared, modified with Sn, and then studied for the electrocatalytic N_2ORR in acidic media by CV to understand the role of surface structure at the Pd/Sn interface. TEM images confirmed the preparation of NCs. The Sn modification increases the N_2ORR activity of NCs. The Sn modification could suppress the H-adsorption at Pd(100) surfaces of the NCs, resulting in the enhancement of the N_2ORR activity.

In conclusion, it was demonstrated that the enhancement of NO_3^- and N_2O adsorption and/or suppression of H-adsorption is necessary at the electrode surface for the improvement of the NO_3RR and N_2ORR in acidic media. The trimetallic PtPd/Sn interface can highly modulate such competitive adsorption processes, resulting in the high NO_3RR and N_2ORR activity. Furthermore, the Pd/Sn interface of Sn-modified Pd NCs improved N_2ORR activity more than unmodified Pd NCs through the suppression of H-adsorption. The findings of this thesis will lead to the development of the highly efficient interfaces between Pt–Pd mixture/alloy NPs and Sn or shape-controlled Pt–Pd mixture/alloy NPs and Sn for the modulation of the NO_3^-, N_2O, and H-adsorption processes.